The Chemistry on Diterpenoids in 1979. Part-I (Special Issue on Polymer Chemistry, Including Organic Chemistry, XV)

AUTHOR(S):

Fujita, Eiichi; Fuji, Kaoru; Nagao, Yoshimitsu; Ochiai, Masahito

CITATION:

Fujita, Eiichi ...[et al]. The Chemistry on Diterpenoids in 1979. Part-I (Special Issue on Polymer Chemistry, Including Organic Chemistry, XV). Bulletin of the Institute for Chemical Research, Kyoto University 1980, 58(4): 484-510

ISSUE DATE:

1980-09-30

URL:

http://hdl.handle.net/2433/76905

Bull. Inst. Chem. Res., Kyoto Univ., Vol. 58, No. 4, 1980

Review

The Chemistry on Diterpenoids in 1979. Part-I[1]

Eiichi FUJITA*, Kaoru FUJI, Yoshimitsu NAGAO,
and Masahito OCHIAI

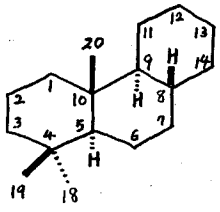
Received April 1, 1980

KEY WORDS: Diterpenoids/ Synthesis/ Structure determination/

I. INTRODUCTION

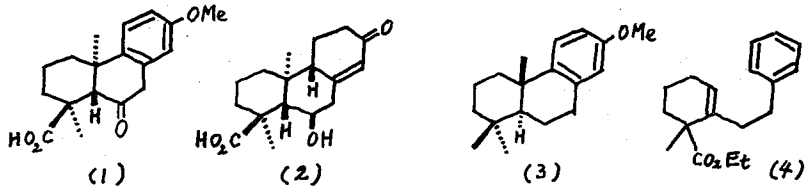
This is one of a series of our annual reviews on diterpenoid chemistry. The classification of the compounds is the same as that used in our reviews since 1969. This review covers literature published from January to June 1979 and also omissions in the previous reviews.

II. PODOCARPANE DERIVATIVES



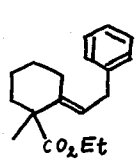
Podocarpane

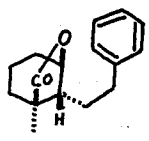
The synthesis of acid **1** and its conversion to **2** were published.[2] (+)-13-Methoxypodocarpa-8,11,13-triene (**3**) was synthesized from (−)-α-cyclocitral.[3] The acid catalyzed cyclialkylation reaction of olefins **4** and **5**, and epimeric lactones **6** and **7** were reported.[4] The acid catalyzed rearrangement of alcohol **8** was reported.[5]

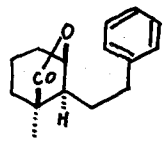


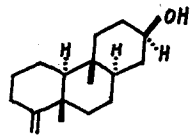
(1) (2) (3) (4)

* 藤田栄一, 冨士　薫, 長尾善光, 落合正仁：Laboratory of Physiological Activity, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

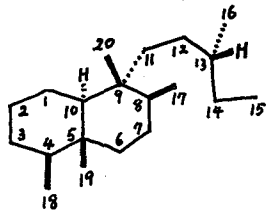

(5)


(6)


(7)

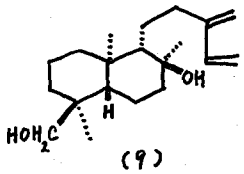

(8)

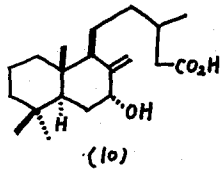
III. LABDANE DERIVATIVES

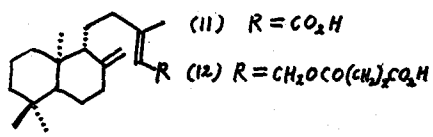


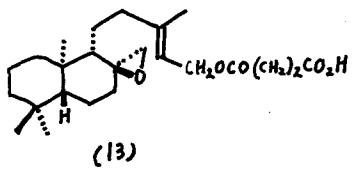
Labdane

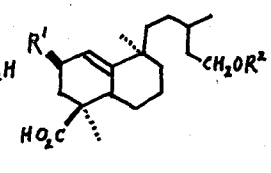
6-Deoxyandalusol (**9**) was isolated from *Sideritis arborescens*.[6] Salvic acid (**10**) was isolated from *Eupatorium salvia*.[7] One known (**11**) and two new diterpenoids, **12** and **13**, were isolated from *Relhania acerosa*.[8] (See also section IV.)


(9)

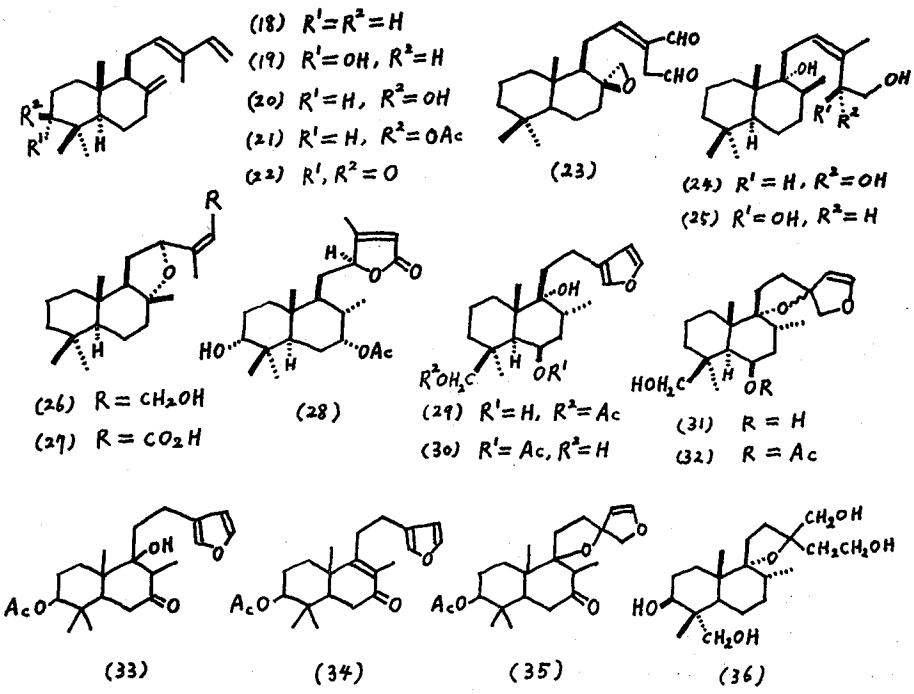

(10)


(11) $R = CO_2H$
(12) $R = CH_2OCO(CH_2)_2CO_2H$


(13)

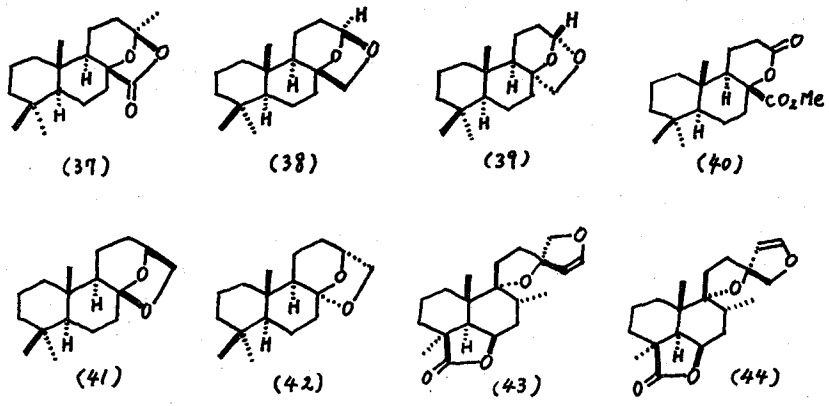

(14) $R' = R^2 = H$
(15) $R' = H,\ R^2 = Ac$
(16) $R' = H,\ R^2 = cinnamyl$
(17) $R' = OH,\ R^2 = H$

Hydrohalimic acid (**14**) and O-acetyl-(**15**), O-cinnamyl-(**16**), and 2β-hydroxyhydrohalimic acids (**17**) were isolated from *Halimium viscosum* as methyl esters.[9] From *Palafoxia rosea* were isolated five new labdane diterpenoids **18**–**22**.[10] (See also section V.) A dialdehyde isolated from *Afromomum daniellii* was shown to have structure **23**.[11] Four labdane diterpenoids **23**–**27** were isolated from *Carterothamnus anomalochaeta*.[12] A novel diterpenoid, evillosin (**28**), was isolated from *Eupatorium villosum*.[13] Besides the known diterpenoids marrubiin and marrubenol, two new acetates **29** and **30** were isolated from *Marrubium sericeum*. Marrubiin and two other new diterpenoids, premarrubenol (**31**) and its acetate **32** were isolated from *M. supinum*.[14] The structures of three new diterpenoids, calyone (**33**), calyenone (**34**), and precalyone (**35**), isolated from *Roylea calycina*, were determined.[15]



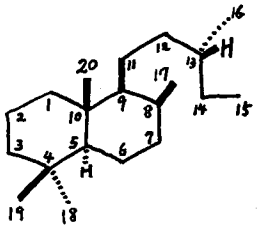
The structures of coleonol-E and -F were reported.[16] The structure and stereochemistry of lagochilin (**36**) was confirmed by its ^{13}C NMR and those of its derivatives.[17] Carbon-13 NMR spectra of serveal azido- and amino labdanes were reported.[18]

Compound **37** was obtained by the oxidation of manool.[19] The syntheses of acetals **38** and **39** and of an ester **40** were reported.[20] Acetals **41** and **42** were synthesized from manool.[21] The cyclization reaction of labdane diterpenoids was shown to afford tetracyclic diterpenoids with a new carbon skeleton.[22]



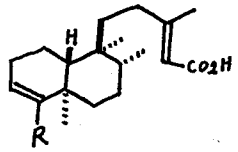
The C-13 epimeric premarrubiins, **43** and **44**, were isolated from *Marbium vulgare* and *Leonotis leonurus*.[23] The structure of acetyl laurifolic acid (13-labden-6α-acetoxy-8α-hydroxy-15-oic acid), isolated from *Cistus laurifolius*, was investigated by an X-ray analysis.[24]

IV. CLERODANE DERIVATIVES

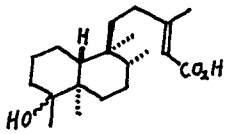


Clerodane

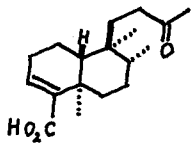
The absolute stereostructures of kolavic acid, kolavenic acid, kolavenolic acid, and kolavonic acid, isolated from *Hardwickia pinnata*, were shown to be **45**, **46**, **47**, and **48**, respectively.[25] The absolute structures of kolavenol (**49**) and kolavelool (**50**) isolated from *H. pinnata* were determined.[26] Compound **51** was isolated from *Relhania acerosa*.[8] (See also section III.)



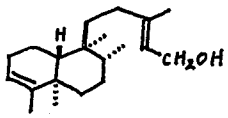
(45) R = CO_2H
(46) R = Me



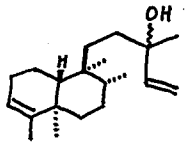
(47)



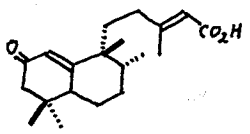
(48)



(49)

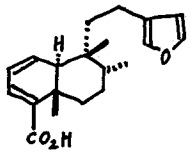


(50)

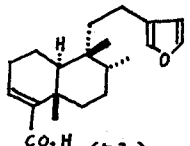


(51)

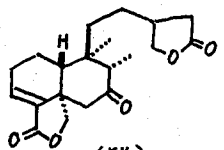
Hardwickiic acid was isolated from *Croton californicus*.[27] The known diterpenoids, **52** and **53** were isolated from *Centipeda orbicularis*.[28] (See also section XV). A new diterpenoid **54** was isolated from *Baccharis genistelloides*.[29] The isolation and structure determinations of two new dilactones **55** and **56** from *Symphiopappus itatiayensis* were reported.[30] The structures of plaunol A (**57**) and B (**58**) isolated from *Croton sublyratus* were established by means of X-ray analysis and chemical correlation.[31]



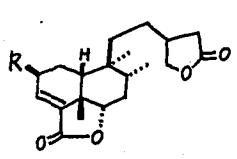
(52)



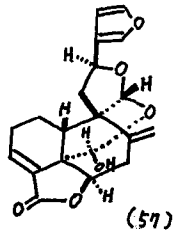
(53)



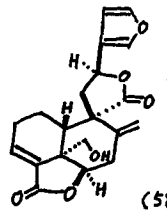
(54)



(55) R = H
(56) R = OH

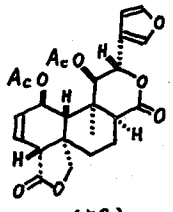


(57)

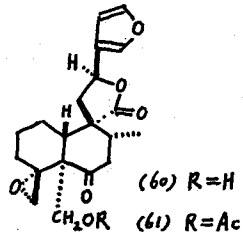


(58)

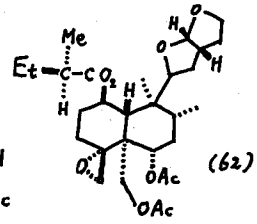
Teuflin, isolated from *Teucrium flavum*, was shown by X-ray analysis to be a C-10 epimer of teucvidin.[32] Splendidin, isolated from *Salvia splendens*, was shown to have structure **59**.[33] New furanoid diterpenoids, gnaphalin (**60**) and its acetate **61** were isolated from *Teucrium gnaphalodes*.[34] The structure of ajugareptansin (**62**), isolated from *Ajuga reptans*, was elucidated by chemical and spectral means and confirmed by X-ray analysis of the corresponding *p*-bromobenzoate.[35] From X-ray analysis the absolute configuration of clerodin was revised to **63** and the structure of 3-epicaryoptin (**64**) was determined.[36] A new diterpenoid strictic acid (**65**) was isolated from *Conyza stricta*.[37]



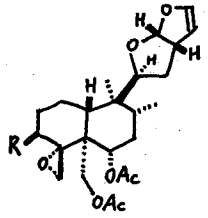
(59)



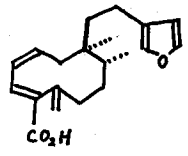
(60) R=H
(61) R=Ac



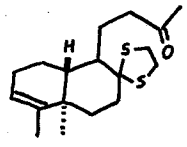
(62)



(63) R = H
(64) R = OAc



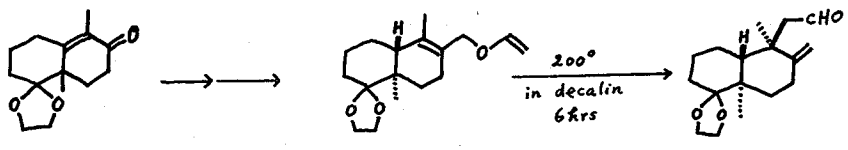
(65)

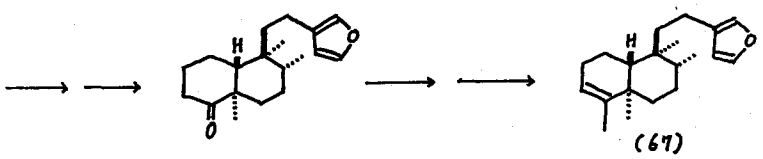


(66)

A synthon **66** for the preparation of clerodane diterpenoids was prepared.[38]

Total synthesis of (±)-annonene (**67**) isolated from *Annona coriacea* was reported. The outline is shown in Chart 1.[39]

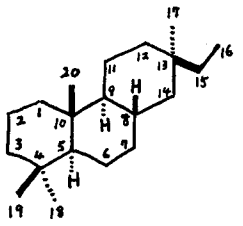




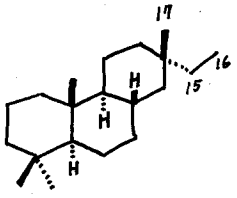
(67)

Chart 1

V. PIMARANE AND ISOPIMARANE DERIVATIVES

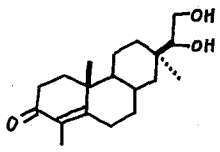


Pimarane

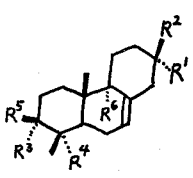


Isopimarane

One known (**68**) and five new (**69**~**73**) diterpenoids were isolated from *Palafoxia resea*.[10] (See also section III.) From *Senecio sandersonii*, alcohols **74** and **75** were isolated.[40] Six diterpenoids **75**~**80** were isolated from *Chrysanthemoides monilifera*.[41]



(68)



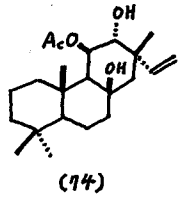
(69) R^1=Me, R^2=  , R^3=OH, R^4=CH_2OH, R^5=R^6=H

(70) R^1=  , R^2=R^4=Me, R^3=R^5=H, R^6=OH

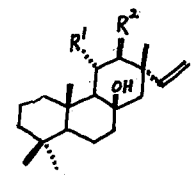
(71) R^1=R^4=Me, R^2=  , R^3=R^6=OH, R^5=H

(72) R^1=R^4=Me, R^2= , R^3=OH, R^5=R^6=H

(73) R^1=R^4=Me, R^2=  , R^3,R^5=O, R^6=H



(74)



(75) R^1=OH, R^2=OAc

(76) R^1=R^2=H

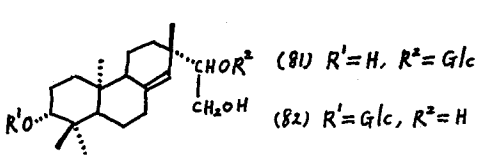
(77) R^1=OH, R^2=H

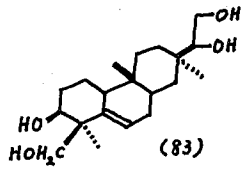
(78) R^1=R^2=OH

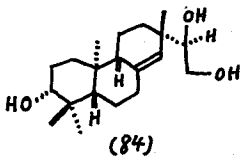
(79) R^1=OAc, R^2=OH

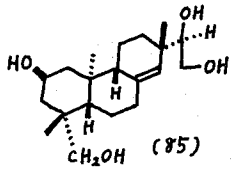
(80) R^1=R^2=OAc

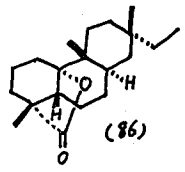
The structure of darutoside, a diterpene glucoside isolated from *Siegesbeckia pubescens*, was revised from **81** to **82**.[42] The carbon-13 NMR spectrum of jesromotetrol (**83**) was investigated with the aid of boric acid induced shifts.[43] The C-15 stereochemistry of darutigenol, aglycon of darutoside, and kirenol, a constituent of *S. pubescens*, was established by means of carbon-13 NMR spectra of their derivatives as shown in formulas **84** and **85**, respectively.[44] The structure of the γ-lactone **86** formed by acid treatment of dihydroisopimaric acid was reconfirmed by X-ray analysis.[45] The ^{13}C NMR spectra were reported on 9 epoxides of methyl esters of resin acids containing the pimarane skeleton.[46]



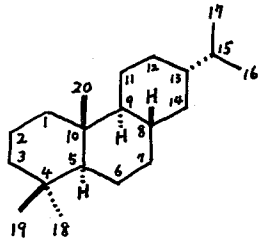

(83)


(84)

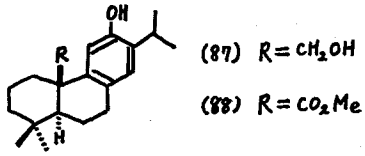

(85)

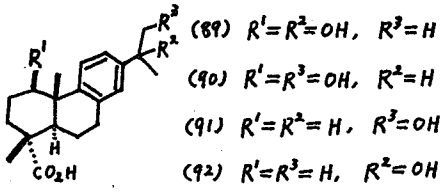

(86)

VI. ABIETANE DERIVATIVES

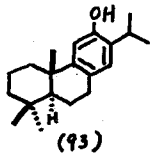

Abietane

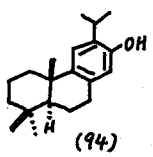
Pisiferol (**87**) and methyl pisiferate (**88**) were isolated from *Chamaecyparis pisifera*.[47] The isolation and identification of acids **89** and **90** formed in incubation experiments of dehydroabietic acid with *Fomes annosus* was reported. Some minor products were tentatively identified as **91** and **92**.[48]

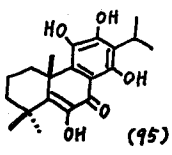

(87) R=CH₂OH
(88) R=CO₂Me

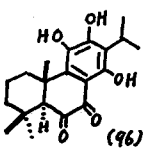

(89) R'=R²=OH, R³=H
(90) R'=R³=OH, R²=H
(91) R'=R²=H, R³=OH
(92) R'=R³=H, R²=OH

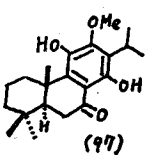
(+)-Ferruginol (**93**) and (+)-sempervirol (**94**) were synthesized from (−)-α-cyclocitral.[3] (See also sections II and XV). The highly-oxygenated diterpenoids, coleon U (**95**) and V (**96**), were synthesized from (+)-ferruginol (**93**).[49] The total syntheses of (+)-inuroyleanol (**97**), (+)-taxoquinone (**98**), (−)-horminone (**99**), (−)-7α-acetoxyroyleanone (**100**), (−)-7-oxoroyleanone (**101**), and (−)-dehydroroyleanone (**102**) were reported.[50]

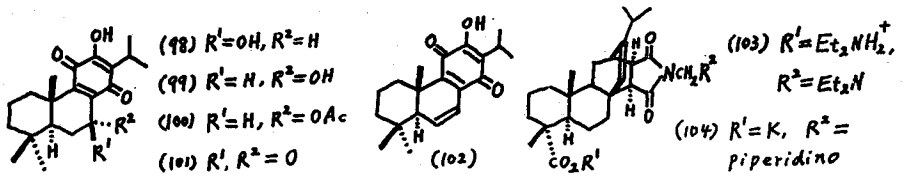

(93)


(94)


(95)


(96)


(97)



The biologically active substances, **103** and **104**, were synthesized from maleopimaric acid.[51] The synthesis of the A ring moiety of triptolide (**105**) was achieved as shown in Chart 2.[52]

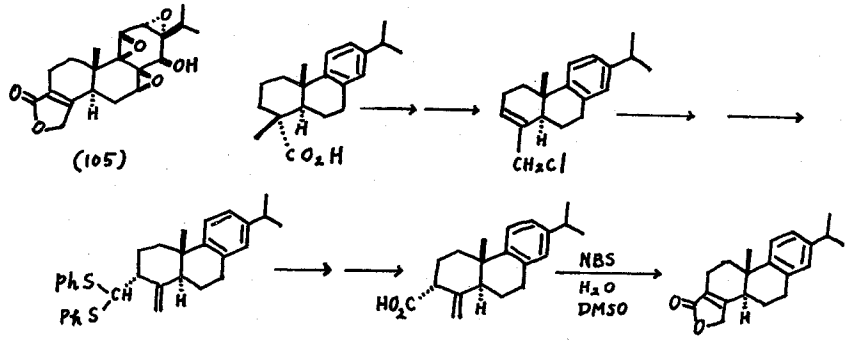
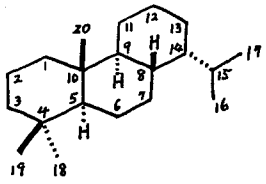


Chart 2

VII. TOTARANE DERIVATIVES



Totarane

The total synthesis of (+)-totarol (**106**) was reported; the outline is shown in Chart 3.[53] Since the conversion of **106** into (+)-podototarin (**107**) had already been reported, this work can be regarded as the total synthesis of (**107**).

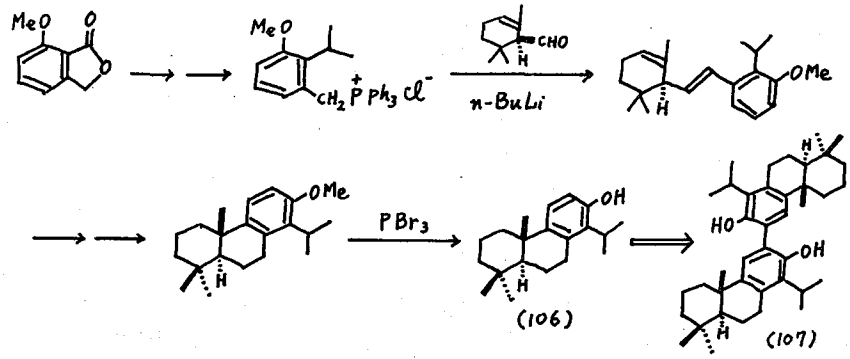
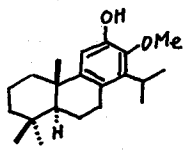
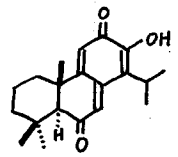


Chart 3

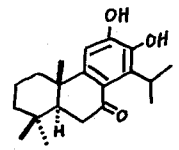
The structure of dispermol was revised to **108**. Maytenoquinone (**109**), dispermone (**110**), and dispermol (**108**) were synthesized.[54]



(108)



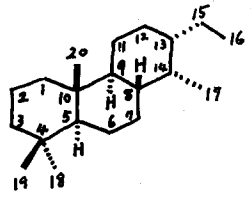
(109)



(110)

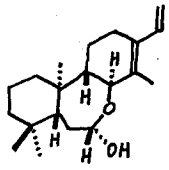
Antitumor activity of 32 kinds of totarane-type norditerpenoid dilactones was reported.[55]

VIII. CASSANE DERIVATIVES

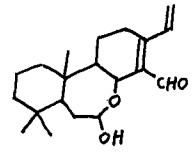


Cassane

The structures of two new diterpenoids isolated from *Acacia jacquemontii* were determined as **111** and **112**, from chemical and spectral evidence; Single crystal X-ray analysis of **111** confirmed the structure and allowed the relative stereochemistry to be determined.[56]

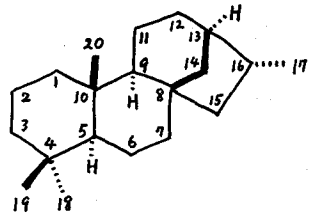


(111)



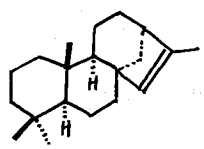
(112)

IX. KAURANE DERIVATIVES

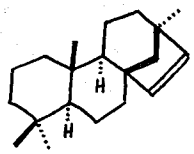


Kaurane

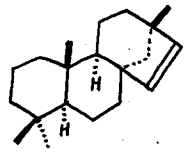
Cupressene, as originally isolated from *Cupressus macrocarpa*, was shown to be a 1: 2 mixture of (+)-isophyllocladene (**113**) with (+)-isohibaene (13α-beyer-15-ene) (**114**) rather than with (−)-hibaene (beyer-15-ene) (**115**) as previously claimed.[57]



(113)

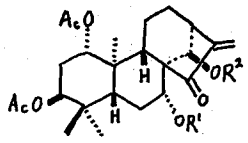


(114)

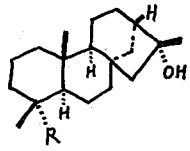


(115)

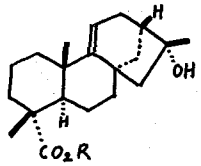
Four new diterpenoids were isolated from the aerial parts of *Isodon shikokianus var. intermedius*. The structures of two of them, shikodokaurin A (**116**) and B (**117**) were established.[58] 13β-Kauranoid diterpenes, **118**～**121** were isolated from *Ruilopezia margarita*.[59]



(116) R^1 = Ac, R^2 = H
(117) R^1 = H, R^2 = Ac

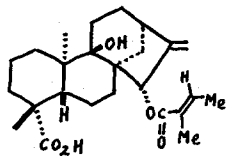


(118) R = CHO
(119) R = Me

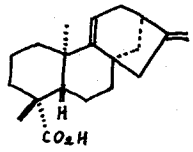


(120) R = H
(121) R = Me

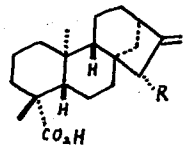
A new kaurenic acid derivative **122** was isolated from *Oyedaea boliviana* with some other known kauranoid diterpenes.[60] Two known kauranoid diterpenes, **123** and **124** were isolated from the aerial parts of *Helichysum platypterum*[61] and of *Polymnia maculata var. maculata*.[62] Kaurenoic acid (**124**) was also obtained from *Stevia setifera*.[63] *ent*-15 β-Tiglinoyloxy-kaur-16-en-19-oic acid (**125**) and kaurenoic acid (**124**) were isolated from *Wedelia scaberrima*.[64]



(122)

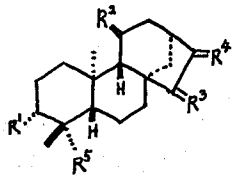


(123)

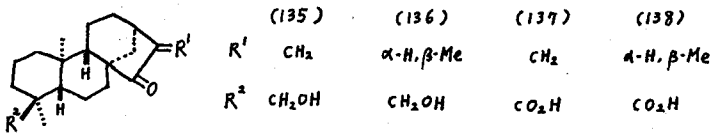


(124) R = H
(125) R = -O-C(=O)-C(H)=C(Me)-Me

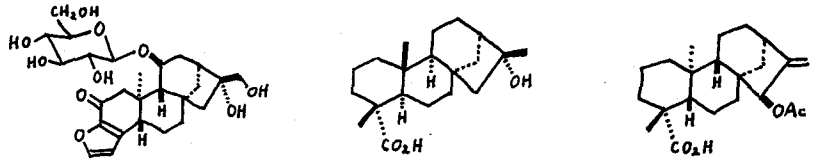
Several known kauranoid diterpenes, **126**～**130** were isolated from *Helichrysum heterolasium*.[65] Four 11-hydroxylated kauranic acids, **131**～**134** were characterized from *Adenostemma lavenia*.[66] Structure determination of the new *ent*-kaurenes, **135**～**138**, isolated along with the three known diterpenoids from *Porella densifolia* was reported.[67]



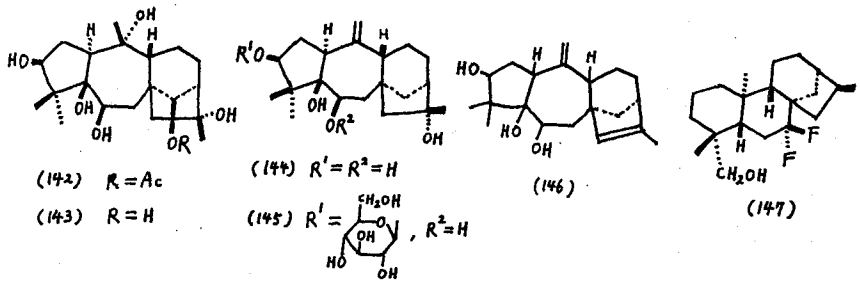
	(126)	(127)	(128)	(129)	(130)	(131)	(132)	(133)	(134)
R^1	H	H	H	H	OAc	H	H	H	H
R^2	H	H	H	OAc	H	OH	OH	OH	OH
R^3	H_2	H_2	α-OAc, β-H	H_2	H_2	α-H, β-OAc	α-H, β-OH	O	O
R^4	CH_2	CH_2	CH_2	CH_2	CH_2	CH_2	CH_2	α-H, β-Me	CH_2
R^5	CHO	CH_2OH	CO_2H	CO_2H	CO_2H	CO_2H	CO_2H	CO_2H	CO_2H



A new furokaurane glycoside was isolated from green coffee-beans and its structure was determined as 11-O-(β-D-glucopyranosyl)cafestol-2-one(**139**).[68] Four kauranoid diterpenes (**118**, **119**, **120**, and **140**) were isolated from the leaves and bud stalks of *Ruilopezia margarita*.[69] The structure of xylopic acid (**141**) isolated from the dried fruits of *Xylopia aethiopica* was established by X-ray analysis.[70]



Grayanotoxin I (**142**) and other substances were isolated as cytotoxic principles from the sap of *Kalmin latifolia*.[71] Subchronic toxicity of the extracts of *Rhododendron* leaves and of their poisonous principles, grayanotoxin I (**142**) and III (**143**) was investigated.[72] From *Leucothoe grayana* a new A-nor B-homo-*ent*-kauranoid, grayanotoxin-XVIII (**144**) and its glucoside (grayanoside B) (**145**) were isolated.[73] The structure of grayathol A, a new diterpene of *Leucothoe grayana*, was determined as **146** except for the absolute configuration.[74] *ent*-7,7-Difluorokauran 19-ol (**147**) was synthesized using the reaction of ketone with diethylaminosulfur trifluoride.[75]



As a synthetic approach to the grayanotoxins and asebotoxins, a new construction of A, B, and C ring system of grayanotoxan was reported.[76] The outline is shown in Chart 4.

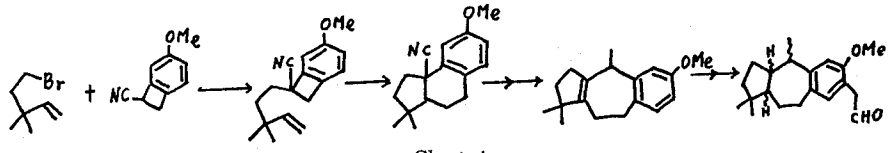
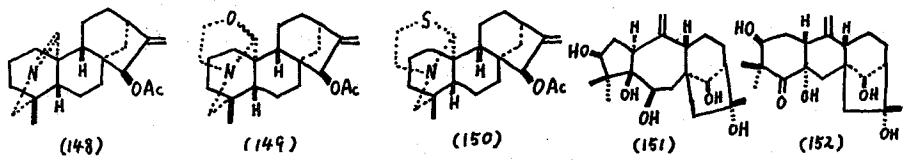


Chart 4

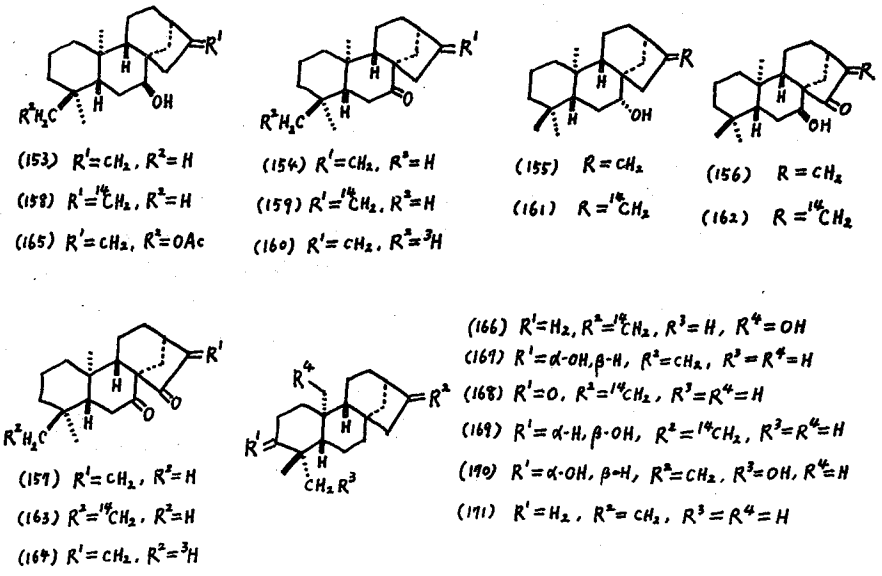
A convenient method for constructing oxazolidine and thiazolidine rings in C_{20}-diterpenoid alkaloid derivatives was reported; treatment of lindheimerine (**148**) with ethylene oxide in glacial acetic acid or in methanol afforded ovatine (**149**) in high yield. When **148**

was treated with excess of neat ethylene sulfide, a colorless crystalline thiazolidine ring containing derivative **150** was obtained in high yield.[77] Treatment of grayanotoxin-II (**151**) with palladium acetate in methanol yielded leucothol D (**152**).[78]



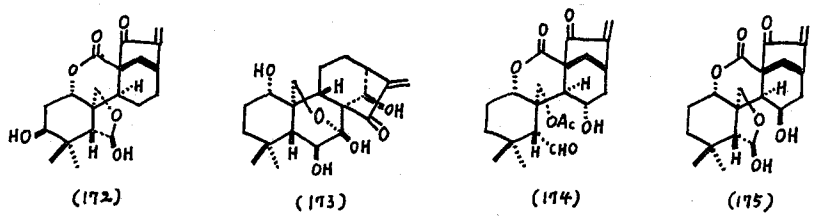
(148) (149) (150) (151) (152)

ent-kaur-16-en-7α-ol (**153**), *ent*-kaur-16-en-7-one (**154**), *ent*-kaur-16-en-7β-ol (**155**), *ent*-15-oxokaur-16-en-7α-ol (**156**), *ent*-kaur-16-ene-7,15-dione (**157**), and the labelled compounds (**158**)～(**164**), were synthesized from epicandicandiol (**165**).[79] *ent*-[17-^{14}C]-kaur-16-en-20-ol (**166**) was synthesized from enmein (**172**), and *ent*-[17-^{14}C] kaur-16-en-3β-ol (**167**), *ent*-[17-^{14}C]kaur-16-en-3-one (**168**), and *ent*-[17-^{14}C]kaur-16-en-3α-ol (**169**) were synthesized from *ent*-kaur-16-ene-3β,19-diol (**170**).[80] These labelled compounds were synthesized for the investigation on the biosynthetic route from *ent*-kaur-16-ene (**171**) into enmein (**172**) and oridonin (**173**) in *Isodon japonicus*.



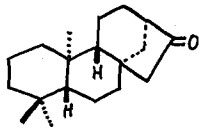
(153) $R'=CH_2$, $R^2=H$
(158) $R'=^{14}CH_2$, $R^2=H$
(165) $R'=CH_2$, $R^2=OAc$
(154) $R'=CH_2$, $R^2=H$
(159) $R'=^{14}CH_2$, $R^2=H$
(160) $R'=CH_2$, $R^2=^3H$
(155) $R=CH_2$
(161) $R=^{14}CH_2$
(156) $R=CH_2$
(162) $R=^{14}CH_2$
(157) $R'=CH_2$, $R^2=H$
(163) $R^2=^{14}CH_2$, $R^2=H$
(169) $R'=CH_2$, $R^2=^3H$
(166) $R'=H_2$, $R^2=^{14}CH_2$, $R^3=H$, $R^4=OH$
(167) $R'=\alpha$-OH,β-H, $R^2=CH_2$, $R^3=R^4=H$
(168) $R'=O$, $R^2=^{14}CH_2$, $R^3=R^4=H$
(169) $R'=\alpha$-H,β-OH, $R^2=^{14}CH_2$, $R^3=R^4=H$
(170) $R'=\alpha$-OH,β-H, $R^2=CH_2$, $R^3=OH$, $R^4=H$
(171) $R'=H_2$, $R^2=CH_2$, $R^3=R^4=H$

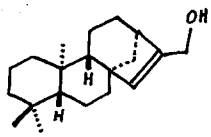
Isodon diterpenoids, enmein (**172**), oridonin (**173**), isodonal (**174**) and nodosin (**175**) exhibited a relatively specific growth inhibitory activity against *Lepidopterous larvae*. These compounds also strongly inhibited the oxidative phosphorylation in mitochondria isolated from silkworm midgut.[81]

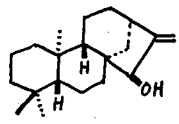


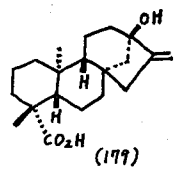
(172) (173) (174) (175)

As the first step towards the biosynthetic studies on grayanotoxins with the aid of ^{13}C isotope, the ^{13}C NMR spectra of grayanotoxin-I (**142**) and -III (**143**) were investigated.[82] Microbial transformations of some kauranoid compounds, **176**~**178**, in the mycelium suspension of *Gibberella fujikuroi* were reported.[83] Metabolism of steviol (**179**) by *G. fujikuroi* was investigated in the presence of plant growth retardant.[84]

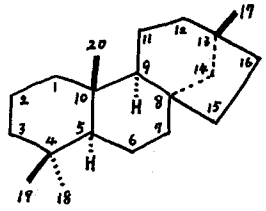

(176)


(177)

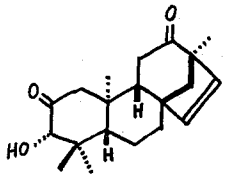

(178)

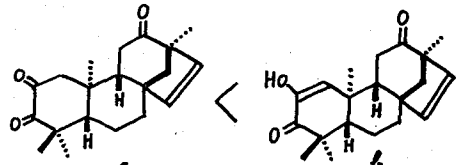

(179)

X. BEYERANE DERIVATIVES

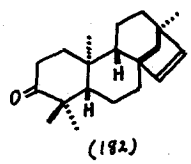

Beyerane

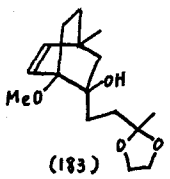
The structures of the major diterpenoid constituents of the heatwood of the Euphorbiaceae *Androstachys johnsonii* were determined as *ent*-3β-hydroxybeyer-15-ene-2,12-dione (**180**) and the corresponding 2,3,12-trione (**181**b<**181**a). Some interesting reactions of the isomeric 2,3-α-ketol acetates derived from **180** and **181** were investigated.[85]

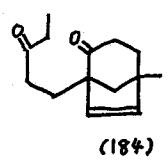

(180)

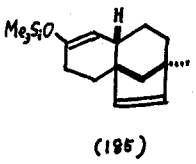

a (181) b

A stereoselective total synthesis of racemic stachenone (**182**) was achieved[86]; the C/D ring synthem bicyclo[3. 2. 1]octenedione (**184**), available from acid-catalyzed rearrangement of the bicyclo[2.2.2]octenol (**183**), was converted into the transfused B-C/D tricyclic derivative **185** by aldol cyclization and dissolving metal reduction. Compound **185** was successively transformed into stachenone (**182**) by Robinson annulation and reductive alkylation.

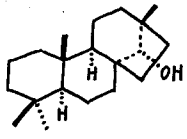

(182)


(183)

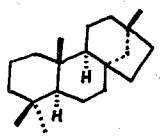

(184)


(185)

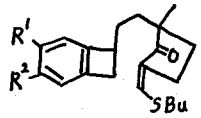
A stereoselective total synthesis of the tetracyclic diterpenes hibaol (**186**) and dihydrohibaene (**187**) was described[87]; thermolysis and desulfurization of 5[(n-butylthio)methylene]-2-[2-(4-methoxybenzocyclobutenyl)ethyl]-2-methylcyclopentanone (**188**) and its analogue **189** gave stereoselectively compound **190** and **191**. Compound **191** was converted into hibaol (**186**). This also constitutes a total synthesis of dihydrohibaene (**187**). In the review article "Total synthesis of natural products by thermolysis", the preparation of hibaol (**186**) was also described.[88]



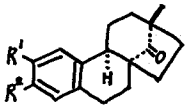
(186)



(187)

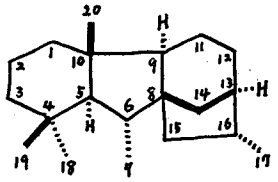


(188) R^1=H, R^2=OMe
(189) R^1=OMe, R^2=H



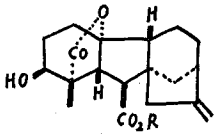
(190) R^1=H, R^2=OMe
(191) R^1=OMe, R^2=H

XI. GIBBERELLANE DERIVATIVES

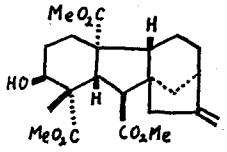


Gibberellane

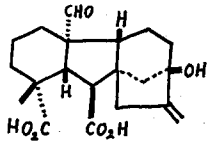
The X-ray structures of gibberellin A_4 methyl ester (**192**) and gibberellin A_{13} trimethyl ester (**193**) were determined.[89] Identification of gibberellins in the rice plant and quantitative changes of gibberellin A_{19} (**194**) throughout its life cycle were reported.[90] Gibberellin A_4 (**195**) produced by *Sphaceloma manihoticola* was characterized as the cause of the superelongation disease of cassava (*Manihot esculenta*).[91]



(192) R=Me
(195) R=H

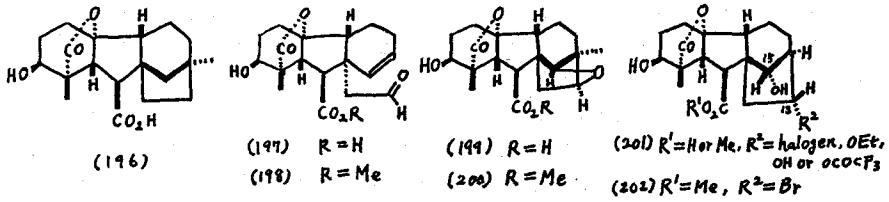


(193)

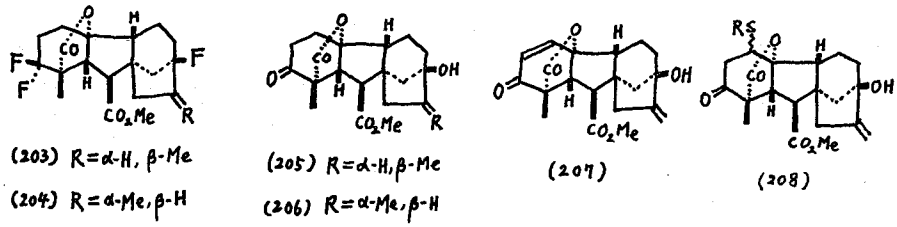


(194)

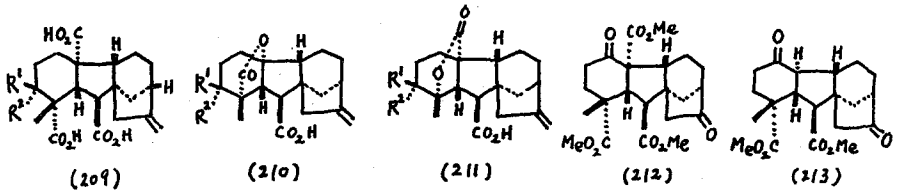
The n→π^* photochemistry of saturated diterpenoid ketones of the gibberellin C type **196** was investigated. A Norrish type 1 cleavage leading to unsaturated aldehyde **197** and **198**, respectively, took place as the main process. These secoaldehydes upon prolonged irradiation underwent intramolecular "crossed" photocycloaddition to the highly strained oxetanes **199** and **200**. Compound **200** was effectively utilized to prepare 13α,15α-bifunctionalized compounds **201**.[92] The X-ray analysis of the gibberellin bromohydrin **202**, which was derived from **200** by the proton catalyzed nucleophilic ring cleavage, was performed.[93]



Trifluorogibberellane derivatives **203** and **204** were prepared by treatment of compounds **205** and **206** with diethylaminosulfur trifluoride.[75] 3-Dehydrogibberellin A_3 methyl ester **207** was treated with RSH (R=H, Pr, $CH_2CH_2NH_2$, CH_2CH_2SH, CH_2CH_2OH, CH_2CO_2H) in CH_2Cl_2-pyridine to give epimeric adducts (**208**).[94]



The removal of C-20 in gibberellins was reported; oxidative decarboxylation of *ent*-gibberellane-19,20-dioic acids (**209**) with lead tetra-acetate yielded mixtures of 19,10-lactones **210** and 20,4-lactones **211**. Methyl *ent*-1,16-dioxo-17-norgibberellane-7,19,20-trioate (**212**) was treated with lithium iodide to afford a 20-norgibberellane **213** with a *trans* A–B ring fusion.[95]



A convergent method to prepare the compound **214** having tetracyclic carbon skelton characteristic of gibberellins was reported.[96] The preparation route is shown in Chart 5.

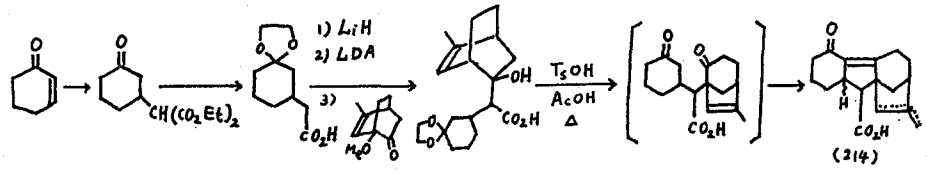
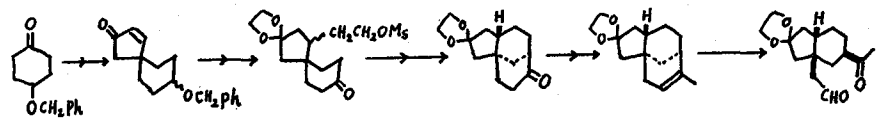


Chart 5

A new and effective route to a key tricyclic intermediate **215** for the total synthesis of gibberellic acid (**216**) was established.[97] The synthetic route is summarized in Chart 6.



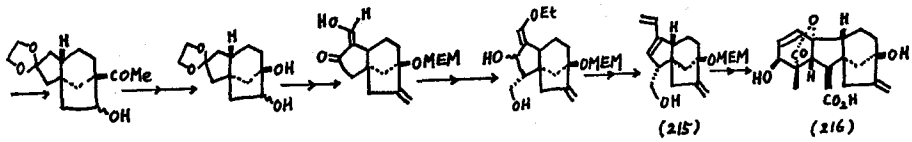


Chart 6

An efficient synthesis of compound **217** was reported; this is a new strategy for gibberellin synthesis.[98] The sequence is illustrated in Chart 7.

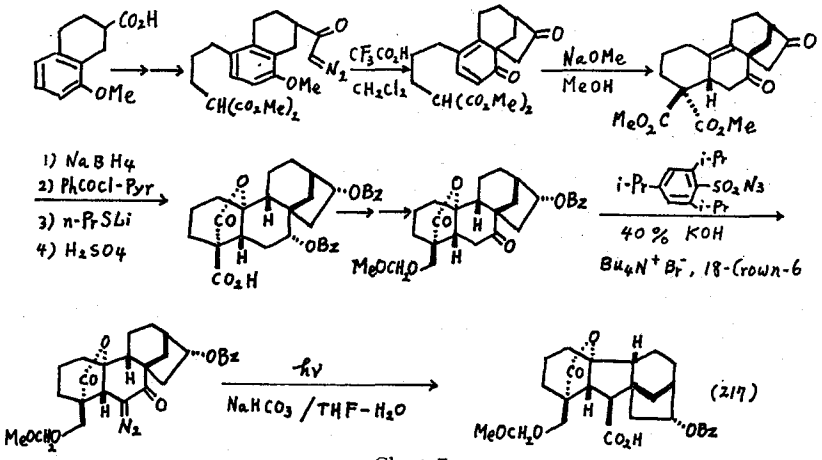
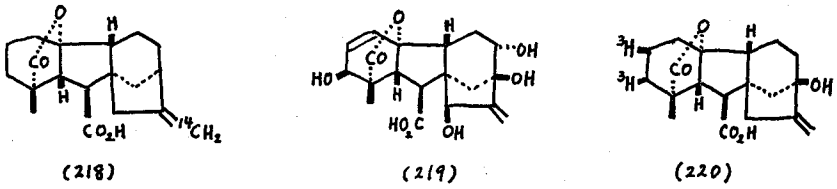


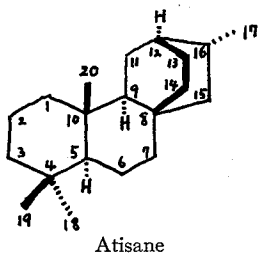
Chart 7

A paper titled "Natural materials as model of synthesis. Concepts and results in the gibberellin phytohormone group" was published.[99] [17-^{14}C]Gibberellin A_9 (**218**) was prepared by introducing ^{14}C into GA_9-17-norketone by the Wittig reaction.[100] A polar gibberellin which was active in the dwarf rice (*Oryza sativa.*) seedling and barley (*Hordeum vulgare*) half-seed assays was extracted from immature sour cherry (*Prunus cerasus*) and identified as gibberellin A_{32} (**219**) by gas-liquid chromatography and selected ion monitoring.[101] Metabolism of tritiated gibberellin A_{20} (**220**) in immature seeds of dwarf pea (*Pisum sativum*) was investigated.[102]



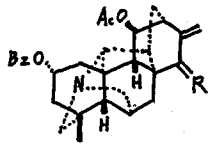
Uptake and distribution of gibberellin A_1 in the short-day plant *Lemna paucicostata* were reported.[103] The biological activities of some iodinated gibberellins were described.[104]

XII. ATISANE DERIVATIVES



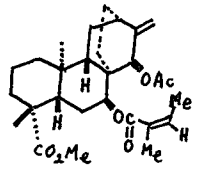
Atisane

Two new atisane-type alkaloids, 11-acetylisohypognavine (**221**) and diacetylisohypognavine (**222**) were obtained together with several aconane type alkaloids, in the course of reinvestigation of the alkaloid constituents of *Aconitum japonicum* of Mt. Takao (Tokyo).[105] A new diterpene, margotianin (**223**) was isolated from *Margotia gummifera*.[106] The crystal structure of atidine (**224**) was determined.[107]

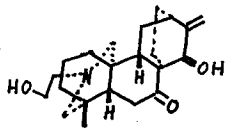


(221) R = H, OH

(222) R = H, OAc



(223)



(224)

Ajaconine (**225**) was rearranged under refluxing in methanol or aq. methanol *via* a "disfavored" 5-endo-trig ring closure to a new, oxazolidine ring-containing compound, 7α-hydroxyisoatisine **226**.[108] (See Chart 8.) Treatment of compound **227** with ethylene oxide in methanol yielded a mixture of atisine acetate **228**, atisine (**229**), and iso atisine (**230**). On treatment with excess of neat ethylene sulfide, compound **226** was converted into a thiazolidine ring containing product **231**.[77]

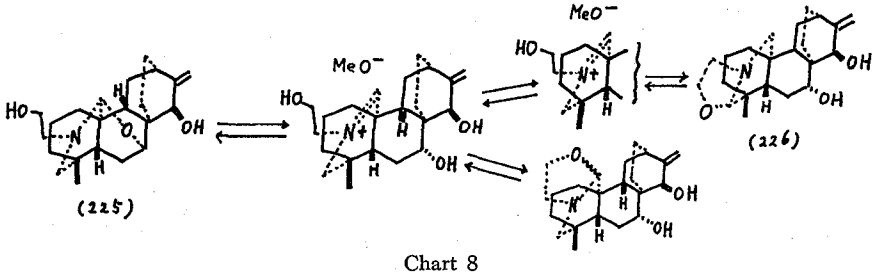
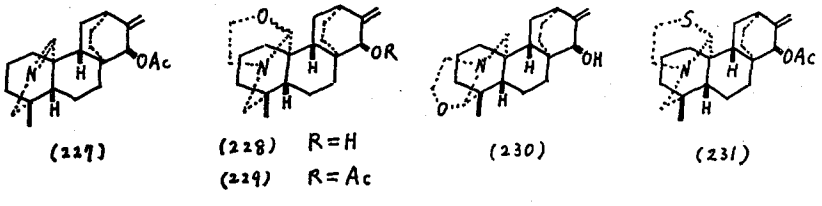


Chart 8



(227) (228) R = H (229) R = Ac (230) (231)

One step synthesis of 1-methyltricyclo[3.2.1.$0^{2,7}$]octan-6-ones was developed by treatment of the α'-enolates of α, β-cyclohexenones with isopropenyltriphenylphosphonium bromide (ITB), which was successfully applied for the synthesis of trachyloban-19-oic acid (**233**) from podocarpic acid (**232**),[109] *via* the sequence shown in Chart 9.

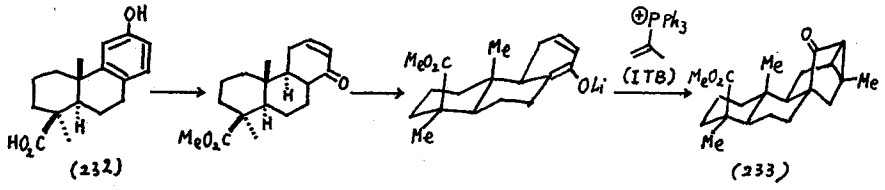
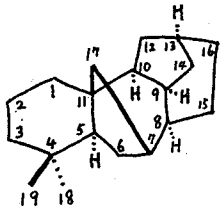


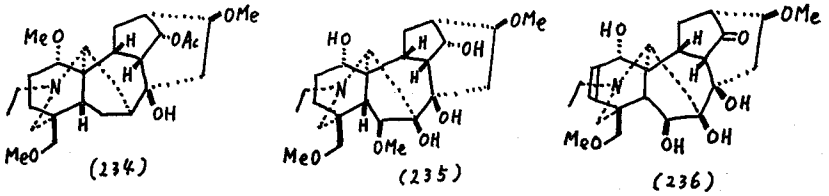
Chart 9

XIII. ACONANE DERIVATIVES

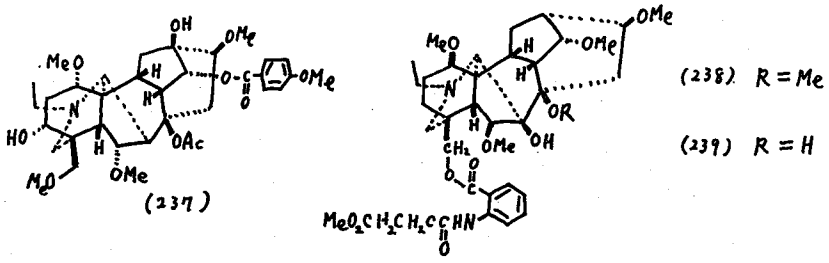


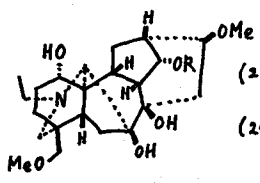
Aconane

New aconane type diterpene alkaloids, 14-acetyltalatizamine (**234**), takaosamine (**235**), and takaonine (**236**) were isolated with several other known alkaloids from *Aconitum japonicum*.[105]



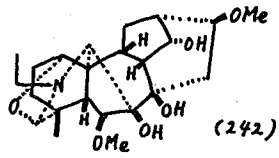
Yunaconitine (**237**) was isolated from *Aconitum hemsleyanum*.[110] Two new diterpene alkaloids, septentrionine (**238**) and septentriodine (**239**) were isolated from *A. septentrionale*.[111] Virescenine (**240**) and 14-acetylvirescenine (**241**), new lycoctonine diterpene alkaloids, were isolated from *Delphinium virescens*.[112] The structure of gadesine (**242**), a new diterpene alkaloid from *D. pentagynum*, was clarified by the X-ray analysis.[113]





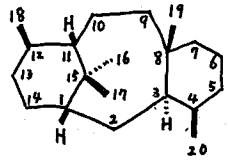
(240) R=H

(241) R=OAc



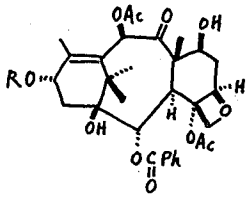
(242)

XIV. TAXANE DERIVATIVES



Taxane

Cephalomannine (**243**), a new antitumor diterpene alkaloid, was isolated from *Cephalotaxus mannii*.[114] It was reported that taxol (**244**) acts as a promoter of calf brain microtubule assembly *in vitro*.[115]

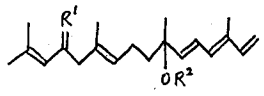


(243) R = -C(=O)-CH(OH)-CH(Ph)-NH-C(=O)-C(=CHMe)-Me

(244) R = -C(=O)-CH(OH)-CH(Ph)-NH-C(=O)-Ph

XV. THE OTHERS

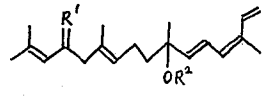
Acyclic diterpenes **245**～**250** were isolated from the marine sponge *Didiscus* sp.[116] Investigation of the aerial part of *Helichrysum calliconum* resulted in the isolation of **251**～**253**.[65] The structure of two biologically active oxepane diterpenes, zoapatanol (**254**) and montanol (**265**) isolated from *Montanoa tomentosa* were determined.[117] Jhanic acid (**256**) was isolated from *Eupatorium jhanii* as its methyl ester.[118] Structure determination of five new diterpenoids **257**～**261** from a soft coral of the genus *Lobophytum* is reported.[119] A new diterpenic acid **262** was isolated from *Centipeda orbicularis*.[28]



(245) R^1=O, R^2=H

(246) R^1=O, R^2=Et

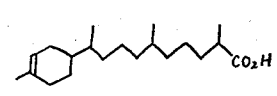
(247) R^1=H_2, R^2=Et



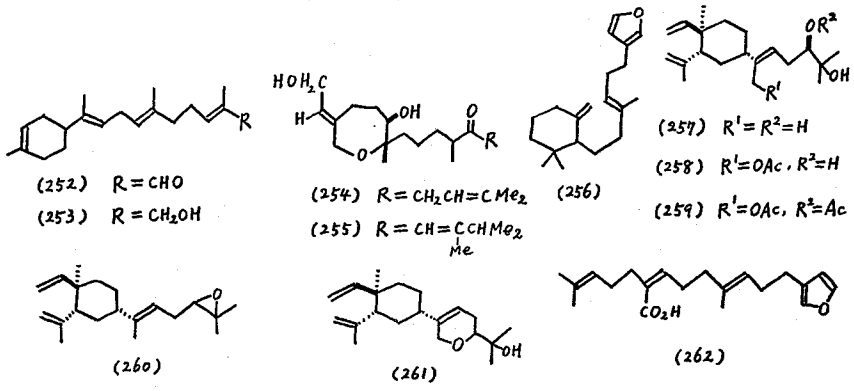
(248) R^1=O, R^2=H

(249) R^1=O, R^2=Et

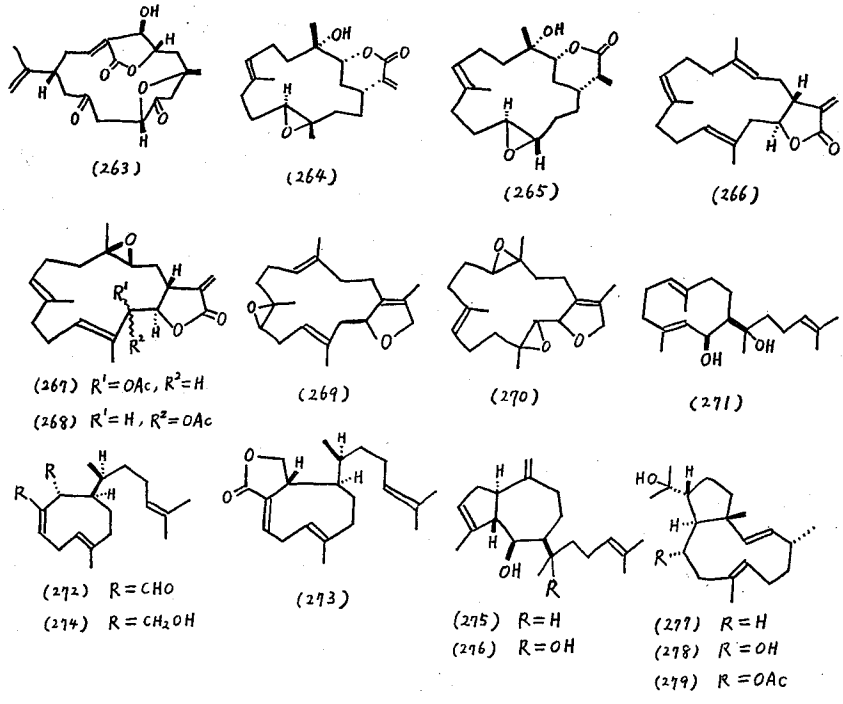
(250) R^1=H_2, R^2=Et



(251)

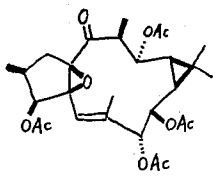


X-ray analyses determined the structures of three marine cembranolides **263**,[120] **264**, and **265**[121] from a soft coral of the genus *Sinularia*. Cembranolides **266**~**268** from *Lobophytum crassospiculatum*[122] and cembranoids **269** and **270** from a *Sarcophyton* species[123] were isolated. The structure elucidation of a new monocyclic diterpenoid, hydroxydilophol (**271**), isolated from *Dictyota masonii* was published.[124] The structures of unusual marine diterpenoids, dictyodial (**272**) and dictyolactone (**273**) were determined by X-ray diffraction experiments on dictyodiol (**274**) and dictyolactone.[125] Investigation of the brown seaweed *Glossophora galapagensis* resulted in the isolation of five known diterpenoides pachydictyol A (**275**), dictyol E (**276**), **277**, **278**, and **279**.[126]

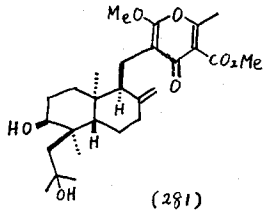


Crystal structure of ingol-3,7,8,12-tetraacetate (**280**) was reported.[127] The structure of a mero-norditerpene, colletotrichin (**281**) isolated from *Colletotrichum capsici* was eluci-

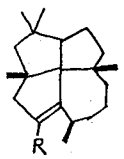
dated by an X-ray analysis of its 3-acetate.[128] The chemistry of a new diterpene, laurenene (**282**), isolated from *Dacrydium cupressinum* was reported.[129] An X-ray analysis of the bromo-derivative **283** confirmed the structure of laurenene.[130] A new minor diterpene, presphaerol (**284**), was isolated from *Sphaerococcus coronopifolius*.[131] A nor-diterpene **285** was isolated from *Vellozia stipitata* and *V. declinans*. Its dehydro derivative **286** was also obtained from *V. declinans*.[132] Hispanonic acid (**287**) and hispaninic acid (**288**) (as its methyl ester) were isolated from *Ballota hispanica*.[133]



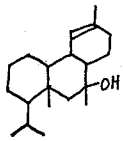
(280)



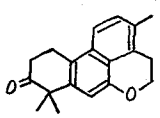
(281)



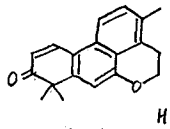
(282) R = H
(283) R = Br



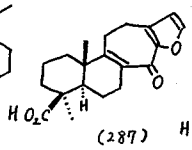
(284)



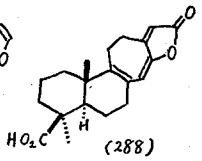
(285)



(286)

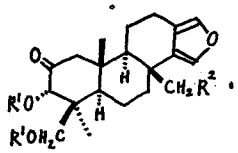


(287)

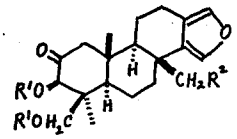


(288)

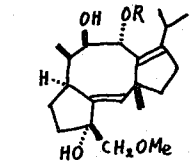
Eight new diterpenes, spongiadiol (**289**), its diacetate (**290**), spongiatriol (**291**), its triacetate (**292**), epispongiadiol (**293**), its diacetate (**294**), epispongiatriol (**295**), and its triacetate (**296**), were found in the dichloromethane extracts of Australian *Spongia* species.[134] Cotylenins H (**297**) and I (**298**) were isolated from the culture filtrate of an unidentified species of *Cladosporium*.[135] X-ray crystallographic studies of fusiccocin deacetylaglycone **299** were reported.[136] An irritant, 12-O-2Z-4E-octadienoyl-4-deoxy-phorbol-13-acetate (**300**) was isolated from *Euphorbia tirucalli*.[137] Jatropholones A (**301**) and B (**302**) were isolated from *Jatropha gossypiifolia* and crystal structure analysis of the latter was performed.[138] The molecular structure of **303** has been determined by means of the X-ray method.[139]



(289) $R^1 = R^2 = H$
(290) $R^1 = Ac$, $R^2 = H$
(291) $R^1 = H$, $R^2 = OH$
(292) $R^1 = Ac$, $R^2 = OAc$

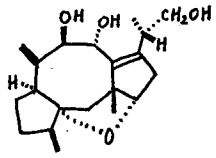


(293) $R^1 = R^2 = H$
(294) $R^1 = Ac$, $R^2 = H$
(295) $R^1 = H$, $R^2 = OH$
(296) $R^1 = Ac$, $R^2 = OAc$

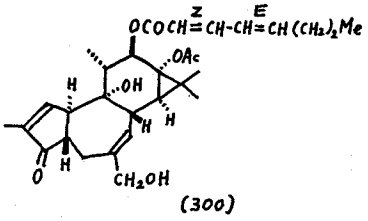


(297) R =

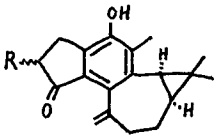
(298) R =



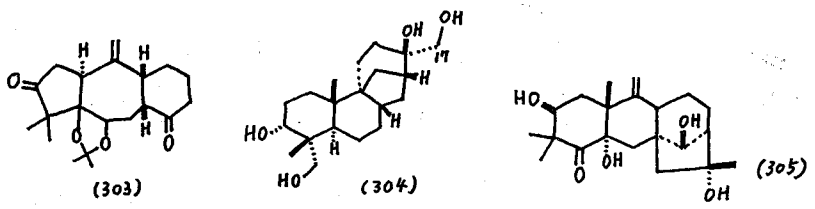
(299)



(300)



(301) R = β-Me
(302) R = α-Me



[17-^{14}C]Aphidicolin and [17-^{3}H]aphidicolin (for the structure of aphidicolin see **304**) were prepared.[140] One step synthesis of leucothol D (**305**) from grayanotoxin-II was reported.[78] Total synthesis of aphidicolin (**304**) has been accomplished by two groups. The outlines are shown in Chart 10 (Trost's group)[141] and Chart 11 (McMurry's group).[142]

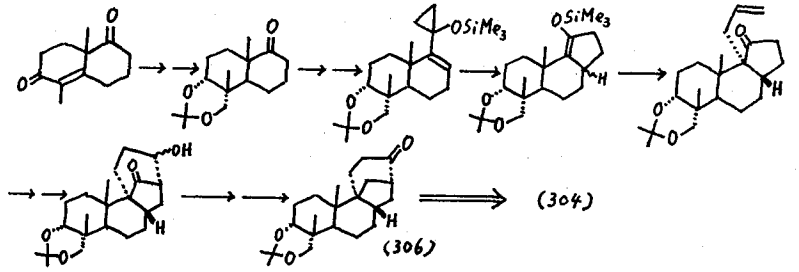


Chart 10

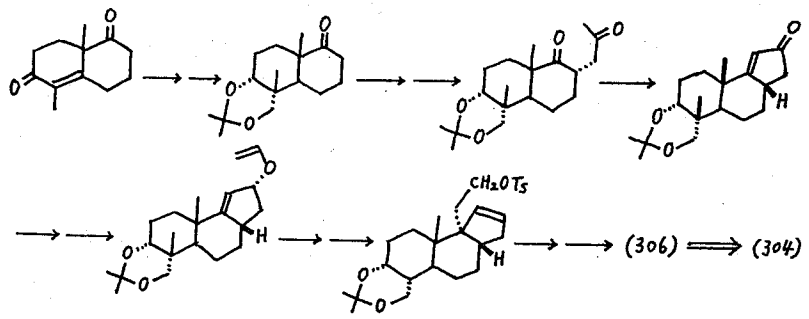
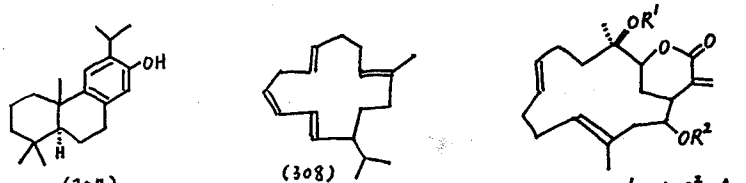
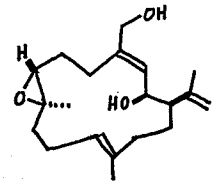
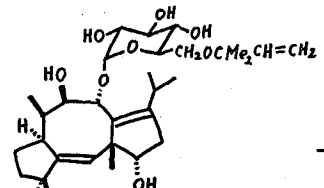


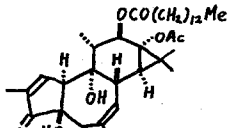
Chart 11

A simple total synthesis of (+)-sempervirol (**307**) has been reported.[3] The acid-catalyzed ring closure of cembrene (**308**) and its derivatives has been studied.[143] A new technique, selective excitation with single frequency off resonance decoupling (SESFORD), was applied to the complete assignment of the ^{13}C NMR spectra of crassin acetate (**309**) and its derivatives **310** and **311**.[144] ^{13}C NMR spectral assignment for asperdiol (**312**) was published.[145] ^{13}C NMR spectra of several cotylenins and fusicoccin (**313**) were also reported.[146]




(312)

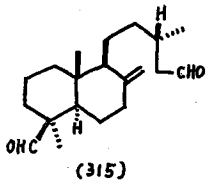

(313)

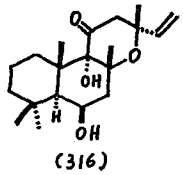

(314)

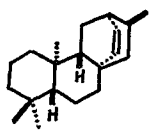
It was reported that 12-O-tetradecanoyl-phorbol-13-acetate (**314**) specifically alters affinity of epidermal growth factor membrane receptors.[147] Systemic promoting action and leukemogenesis in SWR mice by phorbol and structurally related polyfunctional diterpenes were reported.[148] A review article concerned with cubitene was published in Japanese.[149] Another Japanese review article on the biologically active substanes was published and some diterpenoids were cited therein.[150]

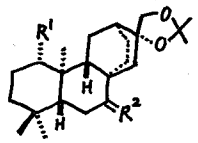
ADDENDA

Junicedral (**315**) and some known diterpenes were isolated from *Juniperus communis* in 1977.[151] Coleosol, a diterpene from the roots of *Coleus forskohlii* was characterized as 6,9-dihydroxyl-11-oxomanoyl oxide (**316**).[152] Methyl dehydroabietate was converted into methyl podocarpate.[153] The ^{13}C NMR of *ent*-atis-13-ene (**317**) and compound **318** were calculated based on the ^{13}C NMR of the bicyclo[3.2.1]- and bicyclo[2.2.2]octanes and *ent*-beyerene compounds. The ^{13}C NMR of **317**～**321** were assigned.[154]

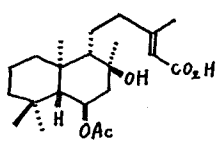

(315)

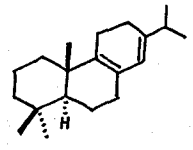

(316)

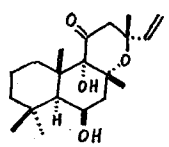

(317)

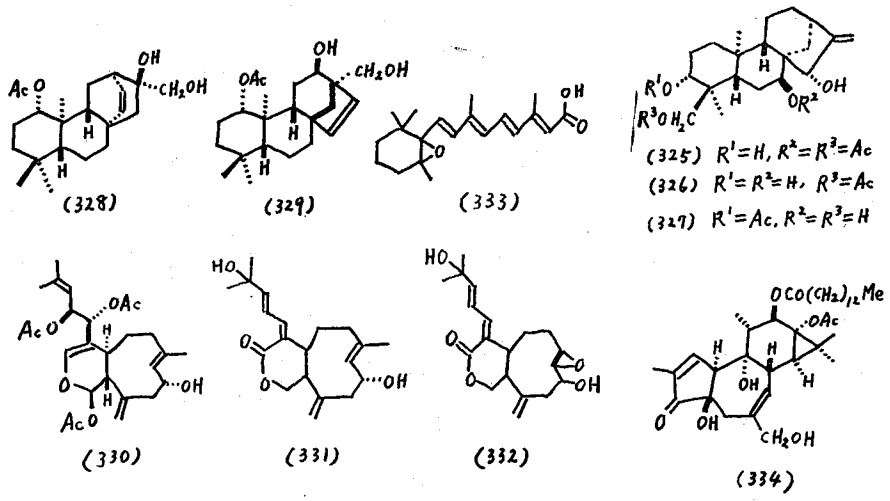

(318) $R^1=H$, $R^2=O$
(319) $R^1=H$, $R^2=H_2$
(320) $R^1=H$, $R^2=\alpha$-H, β-OAc
(321) $R^1=OAc$, $R^2=H_2$

Acetyllaurifolic acid (**322**) was isolated from *Cistus laurifolius* and its structure was determined.[155] Palustradiene (abieta-8,13-diene) (**323**) was isolated from *Juniperus sabina*, and its structure was determined.[156] Coleosol (**324**) was isolated from *Coleus forskohlii* and its structure was determined.[157] New kaurenes, **325**～**329**, were among seventeen diterpenes isolated from *Sideritis crispata, S. Ilicifolia,* and *S. tragoriganum*.[158] Three novel diterpenoids were isolated from the soft coral *Xenia novaebrittaniae* and their structures (**330**～**332**) were determined.[159] It was reported that 5,6-epoxyretinoic acid (**333**) opposes the effect of 12-O-tetradecanoylphorbol-13-acetate (**334**) in bovine lymphocytos.[160]


(322)


(323)


(324)



REFERENCES

(1) For 1978 Part-II, see E. Fujita, K. Fuji, Y. Nagao, and M. Node, *Bull. Inst. Chem. Res., Kyoto Univ.*, **57**, 385 (1979).
(2) A. K. Banerjee, C. D. Ceballo, M. N. Vallejo, and E. H. Bolivar, *Bull. Chem. Soc. Japan*, **52**, 608 (1979).
(3) T. Matsumoto and S. Usui, *ibid.*, **52**, 212 (1979).
(4) U. R. Ghatak, N. R. Chatterjee, and B. Sanyal, *J. Org. Chem.*, **44**, 1992 (1979).
(5) A. K. Banerjee, *Tetrahedron*, **35**, 1247 (1979).
(6) B. Rodriguez and C. Von Carstenn-Lichterfelde, *An. Quim.*, **75**, 110 (1979). (*Chem. Abstr.*, **91**, 57215g [1979].)
(7) M. Hoeneisen, P. G. Sammes, M. Silva, and W. H. Watson, *Rev. Latinoam. Quim.*, **10**, 37 (1979).
(8) F. Bohlmann and J. Jakupovic, *Phytochemistry*, **18**, 631 (1979).
(9) J. De Pascual Teresa, J. G. Urones, H. Carrillo Sanchez, and M. A. Gonzalez Munoz, *An. Quim.*, **75**, 140 (1979). (*Chem. Abstr.* **91**, 57216h [1979].)
(10) F. Bohlmann and H. Czerson, *Phytochemistry*, **18**, 115 (1979).
(11) S. F. Kimbu, T. K. Njimi, B. L. Sondengam, J. A. Akinniyi, and J. D. Connolly, *J. C. S. Perkin Trans. I*, 1303 (1979).
(12) F. Bohlmann, C. Zdero, R. M. King, and H. Robinson, *Phytochemistry*, **18**, 621 (1979).
(13) P. S. Manchand, J. F. Blout, T. McCabe, and J. Clardy, *J. Org. Chem.*, **44**, 1322 (1979).
(14) G. Savona, F. Piozzi, L. M. Arânguez, and B. Rodríquez, *Phytochemistry*, **18**, 859 (1979).
(15) O. Prakash, D. S. Bhakuni, R. S. Kapil, G. S. R. S. Rao, and B. Ravindrantha, *J. C. S. Perkin Trans. I*, 1305 (1979).
(16) P. Painuly, S. B. Katti, and J. S. Tandon, *Indian J. Chem., Sect. B*, **18**, 214 (1979).
(17) Z. I. Mavlyankulova, U. N. Zainutdinov, S. I. Mukhamedkhanova, V. B. Leontév, and Kh, A. Aslanov, *Khim. Prir. Soedin.*, 41 (1979). (*Chem. Abstr.*, **91**, 108106g [1979].)
(18) A. Pancrazi and Q. Khuong-Huu, *J. C. S. Perkin Trans. II*, 918 (1979).
(19) I. M. Godfrey, J. R. Knox, C. L. Raston, and A. H. White, *Austral. J. Chem.*, **32**, 205 (1979).
(20) P. K. Grant, H. T. Liau, and W. A. Temple, *ibid.*, **32**, 1353 (1979).
(21) P. K. Grant and D. D. Rowan, *ibid.*, **32**, 1395 (1979).
(22) P. F. Vlad, N. D. Ungur, and M. N. Koltsa, *Khim. Prirodn. Soedin.*, 581 (1979).
(23) G. Laonigro, R. Lanzetta, M. Parrilli, M. Adinolfi, and L. Mangoni, *Gazz. Chim. Italy*, **109**, 145 (1979). (*Chem. Abstr.*, **91**, 211615w [1979].)
(24) P. Smith-Verdier, F. Florencio, and S. Garcia-Blanco, *Cryst. Struct. Comm.*, **8**, 537 (1979). (*Chem. Abstr.*, **91**, 175550k [1979].)

(25) R. Misra, R. C. Pandey, and S. Dev., *Tetrahedron,* **35,** 979 (1979).
(26) R. Misra, R. C. Pandey, and S. Dev, *ibid.,* **35**, 985 (1979).
(27) D. J. Luzbetak, S. J. Torrance, J. J. Hoffmann, and J. R. Cole, *J. Nat. Prod.* (*Lloydia*), **42**, 315 (1979).
(28) F. Bohlmann and P. K. Mahanta, *Phytochemistry,* **18**, 1067 (1979).
(29) F. Bohlmann, W. Knauf, R. M. King, and H. Robinson, *ibid.,* **18**, 1011 (1979).
(30) W. Vichnewski, R. Murai, and W. Herz, *ibid.,* **18**, 129 (1979).
(31) E. Kitazawa, A. Ogiso, S. Takahashi, A. Sato, M. Kurabayashi, H. Kuwano, T. Hata, and C. Tamura, *Tetrahedron Lett.,* 1117 (1979).
(32) G. Savona, M. P. Paternostro, F. Piozzi, J. R. Hanson, P. B. Hitchcock, and S. A. Thomas, *J. C. S. Perkin Trans. I,* 1915 (1979).
(33) G. Savona, M. P. Paternostro, F. Piozzi, and J. R. Hanson, *ibid.,* 533 (1979).
(34) G. Savona, M. Paternostro, F. Piozzi, and B. Rodriguez, *Tetrahedron Lett.*, 379 (1979).
(35) F. Camps, J. Coll, A. Cortel, and A. Messeguer, *ibid.*, 1709 (1979).
(36) D. Rogers, G. G. Unal, D. J. Williams, V. Ley, G. A. Sim, B. S. Joshi, and K. R. Ravindranath, *J. C. S. Chem. Comm.*, 97 (1979).
(37) S. Tandon and R. P. Rastogi, *Phytochemistry*, **18**, 494 (1979).
(38) J. W. ApSimon and K. Yamasaki, *Polish J. Chem.*, **53**, 107 (1979). (*Chem. Abstr.* **91**, 20790q [1979].)
(39) S. Takahashi, T. Kusumi, and H. Kakisawa, *Chemistry Lett.*, 515 (1979).
(40) F. Bohlmann, C. Zdero, D. Berger, A. Suwita, P. Mahanta, and C. Jeffrey, *Phytochemistry*, **18**, 79 (1979).
(41) F. Bohlmann and M. Grenz, *ibid.*, **18**, 683 (1979).
(42) J. H. Kim, K. D. Han, K. Yamasaki, and O. Tanaka, *ibid.*, **18**, 894 (1979).
(43) W. B. Smith, *J. Org. Chem.*, **44**, 1631 (1979).
(44) E. Wenkert, P. Ceccherelli, M. S. Raju, J. Polonsky, and M. Tingoli, *ibid.*, **44**, 146 (1979).
(45) W. Herz and J. F. Blount, *ibid.*, **44**, 1172 (1979).
(46) B. Delmond, B. Papillaud, J. Valade, M. Petraud, and B. Barbe, *Org. Magn. Reson.*, **12**, 209 (1979). (*Chem. Abstr.* **92** 6730j [1979].)
(47) M. Yatagai and T. Takahashi, *Phytochemistry*, **18**, 176 (1979).
(48) R. Ekman and R. Sjöholm, *Acta Chem. Scand. B*, **33**, 76 (1979).
(49) T. Matsumoto and S. Takeda, *Chemistry Lett.*, 409 (1979).
(50) T. Matsumoto and S. Harada, *Bull. Chem. Soc. Japan*, **52**, 1459 (1979).
(51) A. Kalnins, J. Zandersons, and D. Svikle, *Latv. PSR Zinat. Akad. Vestis*, 108 (1979). (*Chem. Abstr.* **91**, 123894f [1979].)
(52) H. Koike and T. Tokoroyama, *Chemistry Lett.*, 333 (1979).
(53) T. Matsumoto and A. Suetsugu, *Bull. Chem. Soc. Japan,* **52**, 1450 (1979).
(54) T. Matsumoto, T. Ohmura, and S. Usui, *ibid.*, **52**, 1957 (1979).
(55) Y. Hayashi, T. Matsumoto, and T. Tashiro, *Gann* (*Japanese J. Cancer Research*), **70**, 365 (1979).
(56) K. C. Joshi, R. K. Bansal, T. Sharma, R. D. H. Murray, I. T. Forbes, A. F. Cameron, and A. Maltz, *Tetrahedron,* **35**, 1449 (1979).
(57) R. M. Carman and M. D. Sutherland, *Austral. J. Chem.*, **32**, 1131 (1979).
(58) T. Fujita, Y. Takeda, and T. Singu, *Phytochemistry,* **18**, 299 (1979).
(59) A. Usubillaga and T. Nakano, *Planta Med.,* **35**, 331 (1979). (*Chem. Abstr.*, **91**, 74743v [1979].)
(60) F. Bohlmann and C. Zdero, *Phytochemistry,* **18**, 492 (1979).
(61) F. Bohlmann and C. Zdero, *ibid.,* **18**, 641 (1979).
(62) N. Le Van and N. H. Fischer, *ibid.,* **18**, 851 (1979).
(63) F. Bohlmann, L. N. Dutta, W. Dorner, R. M. King, and H. Robinson, *ibid.,* **18**, 673 (1979).
(64) T. C. B. Tomassini and M. E. O. Matos, *ibid.,* **18**, 663 (1979).
(65) F. Bohlmann and W.-R. Abraham, *ibid.,* **18**, 889 (1979).
(66) P. C. Cheng, C. D. Hufford, and N. J. Doorenbos, *J. Nat. Prod.* (*Lloydia*), **42**, 183 (1979).
(67) S. Uto, *J. Sci. Hiroshima Univ., Ser. A: Phys. Chem.*, **43**, 97 (1979).
(68) H. Richter and G. Spiteller, *Chem. Ber.*, **112**, 1088 (1979).
(69) A. Usubillaga and T. Nakano, *Planta Medica,* **35**, 331 (1979).
(70) N. Fiagbe, B. Karlsson, A.-M. Pilotti, and J-E. Berg, *Acta Cryst.*, **B35**, 236 (1979).
(71) S. D. Mancini and J. M. Edwards, *J. Nat. Prod.* (*Lloydia*), **42**, 483 (1979).

(72) H. Hikino, Y. Ohizumi, C. Konno, K. Hashimoto, and H. Wakasa, *Chem. Pharm. Bull.*, **27**, 874 (1979).
(73) J. Sakakibara, N. Shirai, T. Kaiya, and H. Nakata, *Phytochemistry*, **18**, 135 (1979).
(74) A. Furusaki, S. Gasa, N. Hamanaka, R. Ikeda, and T. Matsumoto, *Chemistry Lett.*, 665 (1979).
(75) K. Boulton and B. E. Cross, *J. C. S. Perkin Trans. I*, 1354 (1979).
(76) T. Kametani, M. Tsubuki, H. Nemoto, and K. Fukumoto, *Chem. Pharm. Bull.*, **27**, 152 (1979).
(77) S. W. Pelletier, J. Nowacki, and N. V. Mody, *Synth. Comm.*, **9**, 201 (1979).
(78) T. Kaiya, N. Shirai, and J. Sakakibara, *J. C. S. Chem. Comm.*, 431 (1979).
(79) T. Fujita, S. Takao, and E. Fujita, *J. C. S. Perkin Trans. I*, 910 (1979).
(80) T. Fujita, I. Masuda, S. Takao, and E. Fujita, *ibid.*, 915 (1979).
(81) M. Taniguchi, M. Yamaguchi, I. Kubo, and T. Kubota, *Agr. Biol. Chem.*, **43**, 71 (1979).
(82) T. Matsutani, K. Kawazu, K. Uneyama, S. Torii, and J. Iwasa, *ibid.*, **43**, 631 (1979).
(83) K. Wada, T. Imai, and K. Shibata, *ibid.*, **43**, 1157 (1979).
(84) N. Murofushi, S. Nagura, and N. Takahashi, *ibid.*, **43**, 1159 (1979).
(85) L. P. L. Piacenza, K. H. Pegel, L. Phillips, and E. S. Waight, *J. S. C. Perkin Trans. I*, 1004 (1979).
(86) S. A. Monti and Y.-L. Yang, *J. Org. Chem.*, **44**, 897 (1979).
(87) T. Kametani, K. Suzuki, H. Nemoto, and K. Fukumoto, *ibid.*, **44**, 1036 (1979).
(88) T. Kametani, *Pure Appl. Chem.*, **51**, 747 (1979).
(89) G. Ellames, J. R. Hanson, P. B. Hitchcock, and S. A. Thomas, *J. C. S. Perkin Trans. I*, 1922 (1979).
(90) S. Kurogochi, N. Murofushi, Y. Ota, and N. Takahashi, *Planta*, **146**, 185 (1979).
(91) W. Rademacher and J. E. Graebe, *Biochem. Biophysic. Res. Comm.*, **91**, 35 (1979).
(92) G. Adam and T. V. Sung, *Tetrahedron*, **35**, 557 (1979).
(93) G. Reck, L. Kutschabsky, G. Adam, and T. V. Sung, *ibid.*, **35**, 839 (1979).
(94) B. Voigt and G. Adam, *Pharmazie*, **34**, 362 (1979).
(95) J. R. Bearder, J. MacMillan, C. van Cartenn-Lichterfelde, and J. R. Hanson, *J. C. S. Perkin Trans. I*, 1918 (1979).
(96) S. A. Monti and S.-C. Chen, *J. Org. Chem.*, **44**, 1170 (1979).
(97) E. J. Corey and J. G. Smith, *J. Am. Chem. Soc.*, **101**, 1038 (1979).
(98) L. N. Mander and S. G. Pyne, *ibid.*, **101**, 3373 (1979).
(99) G. Adam, *Z. Chem.*, **19**, 156 (1979).
(100) J. T. Lin and E. Heftmann, *J. of Labbelled Compds. & Radiopharm.*, **16**, 537 (1979).
(101) M. J. Bukovac, E. Yuda, N. Murofushi, and N. Takahashi, *Plant. Physiol.*, **63**, 129 (1979).
(102) R. C. Durley, T. Sassa, and R. P. Pharis, *ibid.*, **64**, 214 (1979).
(103) I. Al-Shalan and R. Kandeler, *Zeitschr. für Pflanzenphysiol.*, **94**, 257 (1979).
(104) B. Keith, L. M. Srivastava, and N. Murofushi, *Agr. Biol. Chem.*, **43**, 141 (1979).
(105) S. Sakai, H. Takayama, and T. Okamoto, *Yakugaku Zasshi*, **99**, 647 (1979).
(106) B. Rodríguez and M. Pinar, *Phytochemistry*, **18**, 891 (1979).
(107) J. Finer-Moore, N. V. Mody, R. S. Sawhney, and S. W. Pelletier, *Cryst. Struct. Comm.*, **8**, 649 (1979). (*Chem. Abstr.*, **91**, 193478x [1979].)
(108) S. W. Pelletier and N. V. Mody, *J. Am. Chem. Soc.*, **101**, 492 (1979).
(109) R. M. Cory, Y. M. A. Naguib, and M. H. Rasmussen, *J. C. S. Chem. Comm.*, 504 (1979).
(110) S.-Y. Chen, *Hua Hsueh, Hsueh Pao*, **37**, 15 (1979). (*Chem. Abstr.*, **91**, 20833f [1979].)
(111) S. W. Pelletier, R. S. Sawhney, and A. J. Aasen, *Heterocycles*, **12**, 377 (1979). (*Chem. Abstr.*, **91**, 20828h [1979].)
(112) S. W. Pelletier, N. V. Mody, A. P. Venkov, and S. B. Jones, Jr., *ibid.*, **12**, 779 (1979). (*Chem. Abstr.*, **91**, 157953q [1979]).
(113) A. G. González, G. de la Fuente, R. Díaz, J. Fayos, and M. Martínez-Ripoll, *Tetrahedron Lett.*, 79, (1979).
(114) R. G. Powell, R. W. Miller, and C. R. Smith, Jr., *J. C. S. Chem. Comm.*, 102 (1979).
(115) P. B. Schiff, J. Fant, and S. B. Horwitz, *Nature*, **277**, 665 (1979).
(116) B. N. Ravi and D. J. Faulkner, *J. Org. Chem.*, **44**, 968 (1979).
(117) S. D. Levine, R. E. Adams, R. Chen, M. L. Cotter, A. F. Hirsch, V. V. Kane, R. M. Kanojia, C. Shaw, M. P. Wachter, E. Chin, R. Huettemann, P. Ostrowski, J. L. Mateos, L. Noriega, A. Guzmán, A. Mijarez, and L. Tovar, *J. Am. Chem. Soc.*, **101**, 3404 (1979).
(118) A. G. González, J. M. Arteaga, B. M. Fraga, and M. G. Hernandez, *An. Quim.*, **75**, 128 (1979). (*Chem. Abstr.*, **91**, 74736v [1979].)
(119) R. W. Dunlop and R. J. Wells, *Austral. J. Chem.*, **32**, 1345 (1979).
(120) K. E. Turner, B. F. Bowden, G. J. Stokie, and C. J. Howard, *Acta Cryst.*, **B35**, 1283 (1979).

(121) M. B. Hossain, D. van der Helm, J. A. Matson, and A. J. Weinheimer, *ibid.*, **B35**, 660 (1979).
(122) A. Ahond, B. F. Bowden, J. C. Coll, J.-D Fourneron, and S. J. Mitchell, *Austral. J. Chem.*, **32**, 1273 (1979).
(123) B. F. Bowden, J. C. Coll, S. J. Mitchell, and G. J. Stokie, *ibid.*, **32**, 653 (1979).
(124) H. H. Sun and W. Fenical, *J. Org. Chem.*, **44**, 1354 (1979).
(125) J. Finer, J. Clardy, W. Fenical, L. Minale, R. Riccio, J. Battaile, M. Kirkup, and R. E. Moore, *ibid.*, **44**, 2044 (1979).
(126) H. H. Sun and W. Fenical, *Phytochemistry*, **18**, 340 (1979).
(127) H. Lotter, H. J. Opferkuch, and E. Hecker, *Tetrahedron Lett.*, 77 (1979).
(128) R. Goddard, I. K. Hatton, J. A, K. Howard, J. MacMillan, T. J. Simpson, and C. J. Gilmore, *J. C. S. Perkin Trans. I*, 1494 (1979).
(129) R. E. Corbett, D. R. Lauren, and R. T. Weavers, *ibid.*, 1774 (1979).
(130) R. E. Corbett, C. M. Couldwell, D. R. Lauren, and R. T. Weavers, *ibid.*, 1791 (1979).
(131) F. Cafieri, L. De Napoli, E. Fattorusso, M. Piattelli, and S. Sciuto, *Tetrahedron Lett.*, 963 (1979).
(132) A. da C. Pinto, R. Pinchin, D. H. T. Zocher, and C. C. Lopes, *ibid.*, 405 (1979).
(133) B. Rodríguez, G. Savona, and F. Piozzi, *J. Org. Chem.*, **44**, 2219 (1979).
(134) R. Kazlauskas, P. T. Murphy, R. J. Wells, K. Noack, W. E. Oberhänsli, and P. Schönholzer, *Austral. J. Chem.*, **32**, 867 (1979).
(135) A. Takahama, T. Sassa, M. Ikeda, and M. Nukina, *Agr. Biol. Chem.*, **43**, 647 (1979).
(136) S. Cerrini, W. Fedeli, E. Gavuzzo, and F. Mazza, *Acta Cryst.*, **B35**, 644 (1979).
(137) A. D. Kinghorn, *J. Nat. Prod.* (*Loydia*), **42**, 112 (1979).
(138) K. K. Purushothaman, S. Chandrasekharan, A. F. Cameron, J. D. Connolly, C. Labbé, A. Maltz, and D. S. Rycroft, *Tetrahedron Lett.*, 979 (1979).
(139) A. Furusaki, S. Gasa, and T. Matsumoto, *Bull. Chem. Soc. Japan*, **52**, 229 (1979).
(140) S. Ikegami, K. Okano, and H. Muragaki, *Agr. Biol. Chem.*, **43**, 889 (1979).
(141) B. M. Trost, Y. Nishimura, K. Yamamoto, and S. S. McElvain, *J. Am. Chem. Soc.*, **101**, 1328 (1979).
(142) J. E. McMurry, A. Andrus, G. M. Ksander, J. H. Musser, and M. A. Johnson, *ibid.*, **101**, 1330 (1979).
(143) W. G. Dauben, J. P. Hubbell, P. Oberhansli, and W. E. Thiessen, *J. Org. Chem.*, **44**, 669 (1979).
(144) G. E. Martin, J. A. Matson, J. C. Turley, and A. J. Weinheimer, *J. Am. Chem. Soc.*, **101**, 1888 (1979).
(145) G. E. Martin, J. A. Matson, and A. J. Weinheimer, *Tetrahedron Lett.*, 2195 (1979).
(146) T. Sassa and A. Takahama, *Agr. Biol. Chem.*, **43**, 385 (1979).
(147) M. Shoyab, J. E. DeLarco, and G. J. Todaro, *Nature*, **279** ,387 (1979).
(148) V. Armuth, I. Berenblum, W. Adolf, H. Opferkuch, R. Schmidt, B. Sorg, and E. Hecker, *J. Cancer Res. and Clinic Oncology*, **95**, 19 (1979).
(149) I. Sato, *Kagaku no Ryoiki*, **33**, 522 (1979).
(150) S. Yamamura, *Kagaku to Seibutsu*, **17**, 365 (1979).
(151) J. De Pascual Teresa, A. F. Barrero, A. San Feliciano, and I. Sanchez Bellido, *An. Quim.*, **73**, 568 (1977). (*Chem. Abstr.*, **91**, 74740s [1979].)
(152) P. K. Jauhari, S. B. Katti, J. S. Tandon, and M. M. Dhar, *Indian J. Chem., Sec. B.*, **16**, 1055 (1978).
(153) S. W. Pelletier, D. L. Herald, Jr., Y. Ichinohe, H. Sakamaki, M. Tanaka, and Y. Nishi, *J. Indian Chem. Soc.*, **55**, 1163 (1978). (*Chem. Abstr.*, **91**, 193454m [1979.])
(154) A. Lopez, C. Marquez, R. M. Rabanal, S. Valverde, and J. Garcia, *An. Quim.*, **73**, 1100 (1978). (*Chem. Abstr.*, **91**, 91797h [1979].)
(155) J. De Pascual Teresa, J. G. Urones, and F. B. Gonzalez, *ibid.*, **74**, 1540 (1978).
(156) J. De Pascual Teresa, A. F. Barrero, M. C. Caballero, and A. San Feliciano, *ibid.*, **74**, 1093 (1979). (*Chem. Abstr.*, **91**, 74741t [1979].)
(157) P. K. Jauhari, S. B. Katti, J. S. Tandon, and M. M. Dhar, *Indian J. Chem., Sect. B*, **16B**, 1055 (1978). (*Chem. Abstr.*, **91**, 57214f [1979].)
(158) M. I. Carrascal, R. M. Rabanal, C. Marquez, and S. Valverde, *An. Quim.*, **74**, 1547 (1979). (*Chem. Abstr.*, **91**, 74738x [1979].)
(159) C. J. Braeckman, D. Daloze, B. Tursch, J. P. Declercq, G. Germain, and M. Van Meerssche, *Bull. des Sociétes Chim. Belges*, **88**, 71 (1979).
(160) P. W. Wertz, T. W. Kensler, G. C. Mueller, A. K. Verma, and R. K. Boutwell, *Nature*, **277**, 227 (1979).